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MATERIAL WITH IMPROVED RESISTANCE TO THERMAL AGEING AND
ITS METHOD OF PRODUCTION

DESCRIPTION

Technical field

The present invention relates to a material with improved resistance to thermal ageing, to a method for producing this material, and to the use of this material in the manufacture of high and very high
5 voltage cables.

The material according to the invention is an insulating material which has improved characteristics of resistance to thermal ageing, in particular resistance to thermal ageing by oxidation.

10 This material with improved characteristics of thermal ageing may be used in any device requiring electric insulation, and in particular for very high voltage cables, even at high temperatures.

15 Prior art

The materials used to produce electric insulation cables or devices often contain insulating organic polymers such as polyolefins.

20 The production of materials having improved resistance to thermal ageing, in particular to thermal ageing by oxidation, involves the addition of antioxidants.

Generally, the antioxidants used to stabilize polyolefins are molecules of fairly low molecular
25 weight which tend to migrate towards the outside of the polymer.

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The materials so produced do not resist well to ageing, in particular to thermal ageing by oxidation.

Description of the invention

5 The purpose of the present invention is precisely to provide a material having very high thermal stability over time, in particular against oxidation.

10 The material of the invention is a material with improved resistance to thermal ageing containing a conducting polymer, preferably 10 to 5000 ppm of conducting polymer, dispersed in an insulating polymer and whose heterogeneity size is 0.1 μm or less as observed under electron microscopy.

15 The materials of the invention contain very low levels of conducting polymer, also called conjugate polymer hereinafter, typically from 10 to 5000 ppm, in the doped or undoped state.

20 Advantageously, the insulating polymer may be chosen from among the thermoplastic resins such as the acrylic, styrene, vinyl or cellulose resins or from among the polyolefins, fluorine-containing polymers, polyethers, polyimides, polycarbonates, polyurethanes, silicones, their copolymers or mixtures between homopolymers and copolymers.

25 For example, the insulating polymer may be chosen from among polyethylene, low density polyethylene, high density polyethylene, linear low density polyethylene, polypropylene, ethylene-propylene-diene ^{terpolymer} ~~monomer~~,
 30 fluorine-containing polyvinylidene, ethylene butacrylate or copolymers of ethylene and vinyl acetate, either alone or in a mixture.

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Document US-A-5 254 633 describes a method for producing conducting or non-conducting films or coatings of polyaniline on a substrate and items formed using said method. It sets forth that particle size is
5 not critical and may vary widely for example from 10^{-9} to 10^{-3} cm³.

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The insulating polymer may also be a thermosetting polymer chosen from among the polyesters, epoxy resins or phenol resins.

Advantageously, the conducting polymer has a melting or softening point compatible with its use with the chosen insulating polymer. In addition, the purity of this conducting polymer must be maximum otherwise impurities may affect the voltage resistance characteristics obtained with the materials of the invention. It must be soluble in organic solvents in its doped state (oxidized) or preferably in its undoped state (reduced).

According to the invention, the conducting polymer may be a charge of organic type having a π system of electrons, relocated on at least 7 atoms, on the main chain of the polymer or the branches thereof. This conducting polymer may either be a simple conducting polymer, or a conducting polymer grafted onto an insulating polymer, or a copolymer containing one or more conjugate systems, or any organic molecule sufficiently relocated or having sufficient conductivity of at least approximately $10^{-9} \text{ S.cm}^{-1}$.

Such molecules may, for example, be polypeptides or vitamin A. In respect of polymers, these are advantageously chosen in the group comprising polythiophene, polyalkylthiophenes, polyaniline, polypyrrole, polyacetylene, polyparaphenylene, their derivatives or their mixtures.

The materials of the invention are obtained by a homogeneous mixture of a conjugate polymer and a polyolefin leading to homogeneity on a scale of less than $0.1 \mu\text{m}$. Producing such materials by direct mixing of powders or granules does not lead to obtaining an

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improvement in the ageing properties with conjugate polymer levels in the order of 1000 ppm.

Therefore the invention also provides a method for producing materials having improved resistance to ageing, in particular to thermal ageing by oxidation, characterized in that it comprises the steps consisting of:

- dissolving at least one conducting polymer in an organic solvent, so as to form an impregnating solution,

- impregnating granules formed of an insulating polymer or of a mixture of insulating polymers with said impregnating solution,

- evaporating the solvent so as to obtain granules of insulating polymer coated with a conducting polymer,

- drying said granules,

- extruding or hot mixing said granules to form a homogeneous mixture.

With the method of the invention it is possible to disperse the conjugate polymer in the insulating polymer on almost molecular scale.

Producing the mixtures includes a first impregnation phase of the insulating polymer granules with a solution containing the conjugate polymer. The use of this method leads to obtaining a very good mixture having the required homogeneity, but in no way amounts to a limitation of the invention. Any other method with which it is possible to obtain homogeneous mixtures on a scale of less than 0.1 micron will be suitable.

After evaporating the solvent, the granules of insulating polymer are coated with the organic charge. The granules are then dried in a drying oven and

extruded. The strip obtained is granulated. The granules obtained may be formed by any conventional technique used for insulating polymers such as casting, rolling, injection, extrusion.

5 The structural characteristics of the conjugate polymer such as its conjugation length, average molecular weight, percentage defect in the production line, even at very low levels, have an effect on the thermal stabilisation obtained with the materials of
10 the invention. These characteristics may be controlled by the conditions of synthesis of the conjugate polymer.

According to the method of the invention, the conducting polymer may represent from 10 to 5000 ppm of
15 the insulating polymer.

According to the invention, the insulating polymer and/or the conducting polymer may be the one or those previously cited.

The material of the invention shows very good
20 resistance to thermal ageing, in particular to oxidation, as shown by the illustrative examples below which are non-restrictive, and in the graphs of appended figures 1 and 2.

This material, obtained for example by the above-
25 cited method, may be used in the manufacture of high and/or very high voltage cables.

More precisely, it is possible to replace chemically cross-linkable polyethylene (CCP), currently used in very high voltage cables, by the material
30 obtained with the method of the invention.

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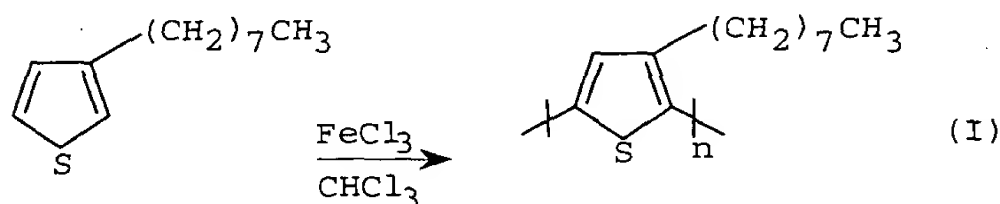
Description of the figures

Figure 1 is a graph showing the change in absorbency at 1715 cm^{-1} (acids and ketones) in relation to thermal oxidation time for a virgin polyethylene and for the same polyethylene stabilized as described in example 1 (PBT FeCl_3) and in example 2 (PBT Magnesium) below.

Figure 2 is a graph showing the change in absorbency at 1715 cm^{-1} (acids and ketones) in relation to thermal oxidation time for a virgin polyethylene and for a stabilised polyethylene as described in example 3 below.

Example 1

Poly(octyl-3 thiophene) (POT) was synthesized by oxidation with ferric chloride in chloroform following the method described by R. SUGIMOTO, S. TAKEDA, H.B. GU, K. YOSHINO, in Chemistry Express, vol. 1, n° 11, pp. 635-638 (1986). The following chemical equation (I) summarizes this synthesis:



The parameters affecting thermal stabilization properties here are the oxidiser over monomer ratio, the solvent and polymerization temperature.

400 mg of the above-cited polymer are dissolved in 200 ml of tetrahydrofuran (THF) so as to obtain the impregnating solution. 200 g of low density polyethylene granules are then added. The solvent is

evaporated at 50°C using a rotary evaporator. A film of conjugate polymer is then deposited on the granules. These granules are dried in a vacuum, at ambient temperature for 24 h. The granules are then extruded. A
5 strip of mixture is obtained using a flat die with a width of 50 mm.

The material is in the form of a clear, brick-red strip containing 2000 ppm POT.

Analysis under scanning electron microscope does
10 not detect any heterogeneity on the scale of 0.1 μm in the material produced in this example.

By way of comparison, the same material made by directly mixing the powder of conducting polymer and the powder of insulating polymer before extrusion,
15 leads to a material whose heterogeneity size is in the order of 0.2 micron.

Measurements of oxidation rate during ageing at 80°C of the material produced in this example were taken at the same time as measurements of oxidation
20 rate during ageing of a virgin polyethylene at 80°C. Ageing was conducted in an oven.

Figure 1 is a graph plotted using these measurements showing the change in absorbency at 1715 cm^{-1} (acids and ketones) in relation to the time of
25 thermal oxidation in hours for a virgin polyethylene (graph referenced 1) and the same polyethylene stabilized as described in this example 1 (graph referenced 3).

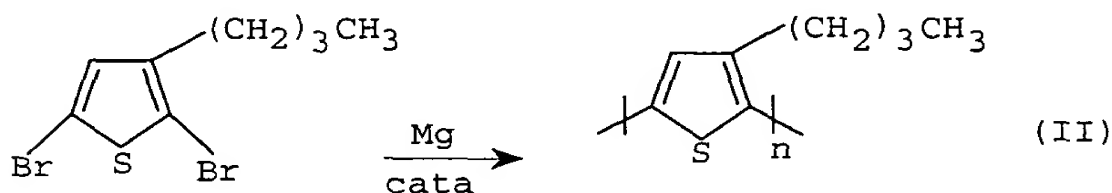
It will be noted from these results, in comparison
30 with the virgin polyethylene, that there is a reduction in oxidation rate during ageing at 80°C for the material of the invention. It is therefore shown that

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with the presence of the conjugate polymer it is possible to stabilize the material.

Example 2

5 Poly(butyl-3 thiophene) (PBT) was synthesized using the general method described by O.INGANAS, W.R. SALANEK, J.E. ÖSTERHOLM, J. LAAKSO in Synthetic Metals, 22, pp. 395-406 (1988) replacing iodine by bromine. The following chemical equation (II) summarizes this
10 synthesis:



Control over synthesis conditions can achieve variation in the characteristics of the material and the final properties of the mixture. For example,
15 molecular weight is dependent upon synthesis conditions and modifies the solubility properties of the conjugate polymer in the matrix in which it is inserted.

The polymer obtained is extruded as in example 1. A clear, orange-coloured strip is obtained containing
20 2000 ppm of PBT.

Analysis under scanning electronic microscope does not reveal any heterogeneity on the scale of 0.1 μm in the material produced in this example.

Measurements were made of the oxidation rate
25 during ageing at 80°C of the material produced in this example. The results of these measurements were used to plot graph 5 in figure 1 previously cited.

From these results it is noted that, in comparison with the virgin polyethylene, there is a reduction in

oxidation rate in relation to time during the ageing at 80°C of the material of the invention. It is therefore demonstrated that with the presence of the conjugate polymer it is possible to stabilize the material. This
5 stabilisation is of the same order as that obtained with the polymer of example one (graph denoted 3 in figure 1).

Examples 1 and 2 therefore show that conjugate polymers derived from thiophene according to the
10 present invention can considerably delay oxidation of the polyethylene. The non-stabilized material starts to deteriorate after 1000 oven hours at 80°C, whereas after 6000 hours the materials of the invention are still not deteriorated at this same temperature.

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Example 3

A mixture containing polyaniline (Pani) and low density polyethylene is made. Polyaniline powder doped with dodecylbenzenesulfonic acid is used, whose
20 production is described for example by Y. CAO, P. SMITH, A.J. HEEGER in Synthetic Metals, 48, pp. 91-97 (1992). This powder is placed in solution in xylene. This solution is used to impregnate the granules following the method of the invention, as in example 1.

25 The granules obtained are extruded as in example 1. A clear, green strip is obtained containing 500 ppm of Pani.

Analysis under a scanning electron microscope does not detect any heterogeneity on the scale of 0.1 μm in
30 the material produced in this example.

Measurements were made of the change in absorbency at 1715 cm^{-1} (acids and ketones) in relation to the time of thermal oxidation in hours ($T=90^\circ\text{C}$, thickness

500 μm) for a virgin polyethylene and a polyethylene stabilised as in this example 3. Appended figure 2 is a graph plotted using these measurements.

The stabilisation of the properties obtained is also of great importance, for harsher ageing, since oxidation of the material of the present invention (graph denoted 7) only occurs on and after 600 hours' ageing at 90°C , whereas oxidation of the virgin polyethylene starts at 50 hours (graph referenced 9).

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Example 4: Manufacture of a high voltage cable

The cable manufactured comprises a conductor core successively coated with an inner semiconductor shield, a material of the invention such as in examples 1 to 3, an outer semiconductor shield and a protective sheath. This cable offers better resistance to ageing by thermal oxidation, even at temperatures of 90°C .

The use of a conjugate polymer in homogeneous mixtures on a scale of $0.1 \mu\text{m}$ or less, which is the subject of the present invention, provides a solution which, in unexpected manner, leads to increasing performance as regards the lifetime of the material subjected to thermal stress.

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